Raman spectroscopic study on NpO[2](+)–Ca(2+) interaction in highly concentrated calcium chloride

AUTHOR(S):

Fujii, Toshiyuki; Uehara, Akihiro; Kitatsuji, Yoshihiro; Yamana, Hajimu

CITATION:

Fujii, Toshiyuki ...[et al]. Raman spectroscopic study on NpO[2](+)–Ca(2+) interaction in highly concentrated calcium chloride. Journal of Radioanalytical and Nuclear Chemistry 2014, 301(1): 293-296

ISSUE DATE:

2014-07

URL:

http://hdl.handle.net/2433/199861

Short Communication

Raman Spectroscopic Study on NpO_2^+-Ca^{2+} Interaction in Highly Concentrated Calcium Chloride

Toshiyuki Fujii[1]*, Akihiro Uehara[1], Yoshihiro Kitatsuji[2], and Hajimu Yamana[1]

*Author to whom correspondence should be addressed

e-mail: tosiyuki@rri.kyoto-u.ac.jp, FAX: +81-72-451-2634

[1] Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University

[2] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency

Abstract

Coordination circumstance of neptunyl ion in concentrated $CaCl_2$ solutions was analyzed by Raman spectrometry. Besides the symmetric stretch (ν_1) mode of NpO_2^+ and NpO_2^{2+}, the asymmetric stretch (ν_3) mode of NpO_2^+ was found. The Raman intensity of the ν_3 mode increased with the concentration of $CaCl_2$ in the system. This would be attributable to the cation-cation interaction between Np(V) and Ca(II).

Keywords

Raman spectrometry, neptunium, neptunyl, calcium chloride, cation-cation interaction

Introduction

The mutual coordination of actinyl ions especially in oxidation state (V) [1] is known as "cation-cation interaction (CCI)". The first evidence of CCI has been found in a complexation of Np(V)-U(VI) [1]. Following it, the CCIs of Np(V) with various cations in aqueous solutions have been found [2-17]. Multiply charged cations [2-8] or oxo-cations [1,9-17] contact with Np(V) dissolved in aqueous solutions as neptunyl ion, NpO_2^+.

Absorption spectrophotometry is the possible analytical method for finding the CCI of Np(V) complexes [1-10,13-15,17]. This technique is effective for the systems containing Np(V) and cations with valence (III) or higher. As divalent cations, only CCIs of Np(V)-Hg(II) and Np(V)-Pb(II) are reported, in which the CCI was not clearly distinguished in absorption spectra [2]. To our knowledge, the CCI between Np(V) and divalent alkaline earth cations has not been found yet.

Another analytical method, Raman spectrometry, is effective for finding the CCI of Np(V) complexes via stretching vibrations of NpO_2^+ [9,12,13]. This method was applied for the pairs of actinyl cations, that is, NpO_2^+-UO_2^{2+}, NpO_2^+-NpO_2^+, and NpO_2^+-NpO_2^{2+}.

Calcium chloride hexahydrate, $CaCl_2 \cdot 6H_2O$, possesses a low melting point, 303 K. The melt is identical with 6.9 mol dm^{-3} (M) and 9.6 mol kg^{-1} (*m*) $CaCl_2$ aqueous solution. Cations, anions, and water molecules in molten hydrate salts, so-called hydrate melts, contact each other continuously by forming a quasi-lattice structure [18]. The coordination circumstance of solute ions dissolved in the media is different from that in water abundant systems, and hence chemical behavior of actinides in concentrated $CaCl_2$ systems is of interest [19,20]. In the present study, we investigated the stretching vibrations of NpO_2^+ in highly concentrated $CaCl_2$ solutions by Raman spectrometry.

The possibility of the CCI between Np(V) and Ca(II) is discussed.

Experimental

Calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$, of analytical grade (Wako Pure Chemical Industries, Ltd.) was used without purification. Weighed amounts of $CaCl_2 \cdot 2H_2O$ and H_2O were mixed for preparing solutions with various concentrations of $CaCl_2$. In order to analyze Np(VI) and Np(V) in the same sample, a nitric acid solution containing ^{237}Np was used as a starting material. A portion of the solution was once dried by heating, where the dried salt is a nitrate of Np(VI) and Np(V), and then the $CaCl_2$ solution prepared was added. The concentration of Np was 0.01 M. The sample volume prepared was 0.2 mL. The sample was taken in a quartz cell with 2 mm light path and the cell was sealed. Electronic absorption spectra of the samples were measured in the wavelength range from 340 to 1350 nm at 0.5 nm intervals by using an UV/Vis/NIR spectrophotometer (Shimadzu, UV-3100PC).

Raman spectra were measured by using a Raman spectrophotometer (NRS-3100, JASCO). A green laser with the wavelength of 531.9 nm was used at the output power of 57.6 mW. The measurement interval of a charge-coupled device (CCD) detector was set to be every 0.3 cm^{-1}. The operations of each 3-seconds measurement were accumulated by 300 times. The experimental temperature was 298 K.

It should be noted that the water activity in hydrate melts is extremely small [19], and the solubility of oxygen in the media is very low [21]. The redox reaction of solutes in the media is hence deeply suppressed [20]. The Raman spectra and absorption spectra of the sealed samples remained the same throughout the experiment. The molar ratio of Np(VI)/Np(V) in our system estimated by using molar absorptivities [22] was 3.

Results and discussion

The literature data of CCIs found for Np(V) are summarized in Table 1. It is clear that absorption spectrophotometry is a powerful tool for finding the CCI of Np(V). The absorption band of NpO_2^+ at *ca*. 980 nm is sensitive to the CCI, which results in a shoulder peak at higher wavelength of the absorption band. Clear increase of absorbance of the shoulder peak has been found for the complexation of NpO_2^+ with VO_2^+ [9], UO_2^{2+} [1,5,10,17], or NpO_2^{2+} [15]. For the CCIs between Np(V) and divalent cations (Hg^{2+} and Pb^{2+}), the two distinct absorption bands were not observed [2]. In the present $CaCl_2$ systems, no shoulder peak was found for the Np(V) absorption band, but a red shift from 985.2 nm to 987.6 nm was found with the increase of $CaCl_2$ concentration.

The Raman spectra obtained are shown in Fig. 1. Three Raman bands were found in the range of 680 to 900 cm^{-1}. Since it was confirmed by absorption spectrophotometry that the samples contain both Np(V) and Np(VI), these Raman bands are assigned to vibrational modes of NpO_2^+ and NpO_2^{2+} species. The Raman frequency of the symmetric stretch (ν_1) mode of hydrated NpO_2^+ is reported to be 766-767 cm^{-1} [9,12,23,24], while that of hydrated NpO_2^{2+} 854-863 cm^{-1} [23-25]. In Fig. 1, the Raman bands at 766-768 cm^{-1} and 835-839 cm^{-1} obtained are assigned to be ν_1 modes of hydrated neptunyl chlorides of Np(V) and Np(VI), respectively.

The complexation of Np(V) with trivalent metal cations via the oxo moiety of NpO_2^+ has been reported in a pioneering work of CCI [2]. The Raman intensity of the band at 802-805 cm^{-1} shown in Fig. 1 clearly increases with the concentration of $CaCl_2$. This suggests that Ca^{2+} contacts with O of NpO_2^+. It is of interest that, in Raman spectroscopic studies on CCI of Np(V)-V(IV) [9] and Np(V)-Np(V) [12,13], the ν_3 band of NpO_2^+ which is not Raman-active was observed. Similar phenomenon may

have occurred in the present study.

The symmetric stretch (ν_1) mode of linear YXY-($\mathbf{D}_{\infty h}$) type molecules is Raman-active while the asymmetric stretch (ν_3) mode of them is infrared-active (not Raman-active) [26]. The ν_3 mode turns to Raman-active for linear YXZ-($\mathbf{C}_{\infty v}$) type molecules [26]. NpO_2^+ possesses two Np=O bonds. If the covalency of two Np=O bonds and/or the apparent mass of two O atoms vary through the complexation of NpO_2^+ with Ca^{2+}, NpO_2^+ would act as a YXZ-($\mathbf{C}_{\infty v}$) type molecule. This means that the ν_3 mode appears in the Raman spectrum. The ν_3 frequency of NpO_2^+ found for the CCI of Np(V)-Np(V) is 37 cm^{-1} larger than its ν_1 frequency [12]. In the present study, the Raman band at 802-805 cm^{-1} is *ca*. 37 cm^{-1} larger than the ν_1 band of NpO_2^+ (766-768 cm^{-1}). The Np concentration of 0.01 M may be too small to found the CCIs of Np(V)-Np(V) [10-14] and/or Np(V)-Np(VI) [1,15,16]. The Raman band found at 802-805 cm^{-1} would hence be the ν_3 band of NpO_2^+ and the increase of its Raman intensity would be attributable to the complexation of Np(V) with Ca^{2+} via the oxo moiety of NpO_2^+.

Conclusions

A Raman band corresponding to the ν_3 mode of NpO_2^+ was found for the highly concentrated $CaCl_2$ system. This would be attributable to the complexation of Np(V) with Ca^{2+} via the oxo moiety of NpO_2^+. Absorption spectrophotometry is not effective for studying the Np(V)-Ca(II) interaction, while Raman spectrometry is useful to find the CCI.

Acknowledgment

This research was partly supported by Grants-in-Aid for Scientific Research (No.

125 23760827) from the Ministry of Education, Culture, Sports, Science and Technology,
126 Japan.

127

128

129

References

[1] Sullivan JC, Hindman JC, Zielen AJ (1961) J Am Chem Soc 83:3373-3378

[2] Sullivan JC (1962) J Am Chem Soc 84:4256-4259

[3] Sullivan JC (1964) Inorg Chem 3:315-319

[4] Rykov AG, Frolov AA (1972) Radiokhimiya 14:717-719

[5] Rykov AG, Frolov AA (1972) Radiokhimiya 14:709-717

[6] Murmann K, Sullivan JC (1967) Inorg Chem 6:892-900

[7] Frolov AA, Rykov AG (1974) Radiokhimiya 16:556-557

[8] Stoyer NJ, Hoffman DC, Silva RJ (2000) Radiochim Acta 88:279-282

[9] Madic C, Begun GM, Hobart DE, Hahn RL (1983) Radiochim Acta 34:195-202

[10] Stout BE, Choppin GR (1993) Radiochim Acta 61:65-67

[11] Skanthakumar S, Antonio MR, Soderholm L (2008) Inorg Chem 47:4591-4595

[12] Guillaume B, Begun GM, Hahn RL (1982) Inorg Chem 21:1159-1166

[13] Grégoire-Kappenstein AC, Moicy Ph, Cote G, Blanc P (2003) Radiochim Acta 91:665-672

[14] Den Auwer C, Grégoire-Kappenstein AC, Moisy Ph (2003) Radiochim Acta 91:773-776

[15] Madic C, Guillaume B, Morisseau JC, Moulin JP (1979) J Inorg Nucl Chem 41:1027-1031

[16] Guillaume B, Hahn RL, Harten AH (1983) Inorg Chem 22:109-111

[17] Xian L, Tian G, Zheng W, Rao L (2012) Dalton Trans 41:8532-8538

[18] Marcus Y (1985) Ion solvation. Wiley, Chichester

[19] Fujii T., Okude G, Uehara A, Sekimoto S, Hayashi H, Akabori M, Minato K, Yamana H (2011) J Radioanal Nucl Chem 288:181-187

[20] Uehara A, Shirai O, Fujii T, Nagai T, Yamana H (2012) J Appl Electrochem

155 42:455-461
156 [21] Millero F J, Huang F, Graham T B (2003) J Soln Chem 32:473
157 [22] Zenko Y, Johnson SG, Kimura T, Krsul JR (2006) In: Morss LR, Edelsen NM,
158 Fugar J, Katz JJ (eds) The chemistry of actinide and transactinide elements, 3rd edn.
159 Springer, Dordrecht
160 [23] Basile LJ, Sullivan JC, Ferraro JR, LaBonville P (1974) Appl Spectrosc 28:142-145
161 [24] Fujii T, Okude G, Uehara A, Yamana H (2010) IOP Conf Ser Mater Sci Eng
162 9:012061(7 pages)
163 [25] Madic C, Begun GM, Hobart DE, Hahn RL (1984) Inorg Chem 23:1914-1921
164 [26] Nakamoto K (1997) Infrared and Raman spectra of inorganic and coordination
165 compounds. John Wiley & Sons, New York
166

167

168 **Table 1** Cations for CCIs of Np(V) in aqueous solutions.

Valence	Cation	Medium	Analytical method[a]	Reference
(II)	Ca^{2+}	Chloride	Raman spectrometry	This study
	Hg^{2+}	Perchlorate	Absorption spectrophotometry	[2]
	Pb^{2+}	Perchlorate	Absorption spectrophotometry	[2]
(III)	Al^{3+}	Perchlorate	Absorption spectrophotometry	[2]
	Sc^{3+}	Perchlorate	Absorption spectrophotometry	[2]
	Cr^{3+}	Perchlorate	Absorption spectrophotometry	[2,3]
	Fe^{3+}	Perchlorate	Absorption spectrophotometry	[2,4,5]
	Ga^{3+}	Perchlorate	Absorption spectrophotometry	[2]
	Rh^{3+}	Perchlorate	Absorption spectrophotometry	[6]
			Infrared spectrometry	
	In^{3+}	Perchlorate	Absorption spectrophotometry	[2,7]
	BiO^{+}	Perchlorate	Absorption spectrophotometry	[2]
(IV)	VO^{2+}	Perchlorate	Absorption spectrophotometry	[9]
			Raman spectrometry	
	Th^{4+}	Perchlorate	Absorption spectrophotometry	[5,8]
		Perchlorate	LIPAS	[8]
(V)	NpO_2^{+}	Perchlorate	Absorption spectrophotometry	[10]
		Perchlorate	HEXS	[11]
		Perchlorate	Raman spectrometry	[12]
		Nitrate	Absorption spectrophotometry	[13,14]
		Nitrate	EXAFS	[14]
		Nitrate	Raman spectrometry	[13]
(VI)	UO_2^{2+}	Perchlorate	Absorption spectrophotometry	[1,5,10,15]
		Perchlorate	Potentiometric measurement	[1]
			Proton relaxation measurement	
		Perchlorate	LAXS	[16]
		Perchlorate	LIPAS	[8]
		Perchlorate	Raman spectrometry	[12],
		Nitrate	Absorption spectrophotometry	[17]
			Microcalorimetry	
	NpO_2^{2+}	Perchlorate	Absorption spectrophotometry	[1,15]
		Perchlorate	Potentiometric measurement	[1]
			Proton relaxation measurement	
		Perchlorate	LAXS	[16]

169 [a] EXAFS: Extended X-ray Absorption Fine Structure, HEXS: High-Energy X-ray Scattering, LAXS:
170 Large-Angle X-ray Scattering, LIPAS: Laser -Induced PhotoAcoustic Spectroscopy.

171

172

173

174

175 **Figure Caption**

176 Fig. 1 Raman spectra of 0.01 M Np in concentrated $CaCl_2$ solutions. Background

177 spectrum was subtracted. Raman intensity was normalized by sum of peak areas.

178

179

180

181

182

183

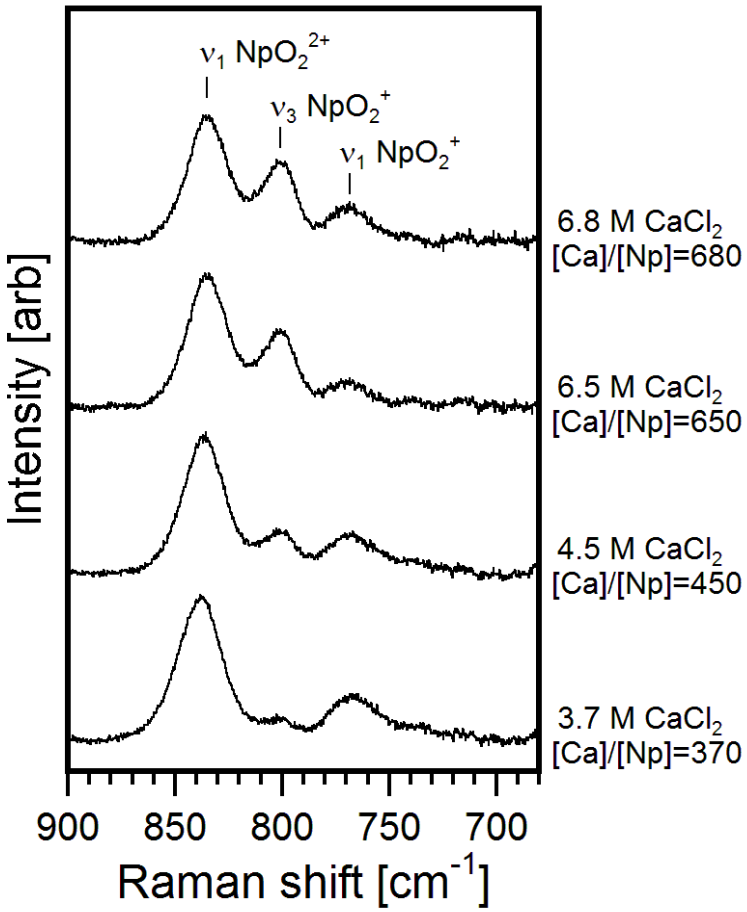

Fig. 1 (T. Fujii et al.)